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Crystallization of supercooled liquid selenium

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With 18 figures in the text

§ 1. **Introduction.** The present paper is one of a series of investigations on the physical properties of selenium. The earlier papers deal with the photoelectric effect (1), resistivity (2), thermoelectric power (3), volume, internal energy, and entropy (4) of amorphous and crystalline selenium. In the present paper various observations and measurements on the types and rate of crystallization of supercooled liquid selenium are given. The alterations of resistivity and optical properties of selenium when changing from the amorphous to the crystalline state make this substance particularly suitable for the study of this transformation process and its kinetics.

The investigation, the results of which will be communicated in the following, has been spread over ten years, and the laboratory work has been performed by several collaborators. Thus the results of § 3 are chiefly due to the work by Andersson and Gullberg, those of §§ 4 and 5 to work begun by Pihlstrand and continued by Gullberg and Glansholm, those of § 6 to work by Glansholm and Ekedahl, and those of §§ 7, 8 and 9 to work by Andersson and Ekedahl.

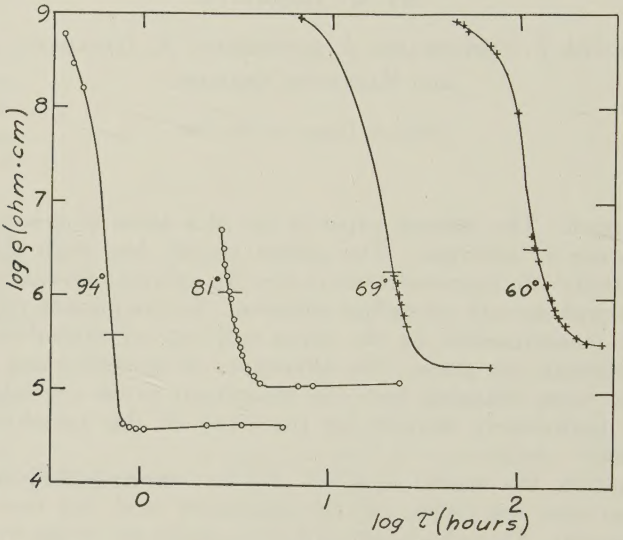
The investigations have been subventioned partly by the Boliden Gruvaktiebolag and partly by grants from the Government through the Board of the Technical Universities and through the Swedish Natural Sciences Research Council. We are much obliged to Professor A. Hultgren and Mr. G. Ericson for good advice and skilful help in the use of metal microscopy.

§ 2. **Selenium specimens.** Most of the following measurements were carried out with five deliveries of Boliden selenium here denoted as Se III, IV, VII, VIII and IX. They contained 99.92, 99.995, 99.99, 99.96 and 99.96% Se respectively. These specimens were either simply molten, stirred in the liquid state, heated in evacuated and sealed glass vessels at different temperatures above the melting point, vacuum distilled, or centrifugated in the liquid state.

The distillation in vacuum was performed in the following way. The selenium was contained in one of two vertical glass tubes, connected together at their upper end. The tubes were kept in a furnace, and the one filled with selenium was heated some fifty degrees above the temperature of the furnace, so that some of the selenium distilled over to the other tube.

Centrifugation was done in a centrifugal machine with a conical aluminium rotator which could be heated to a temperature above the melting point of selenium. Four glass tubes with a length of 70 and an inner diameter of 8 mm containing molten selenium were placed into four holes in the wall of the conical rotator, where they had an inward slope of 45°.

§ 3. **Preliminary studies of the kinetics of crystallization by resistance measurements and thermal analysis.** A preliminary investigation on the kinetics of the crystallization was made by electric resistance measurements. The experimental ar-



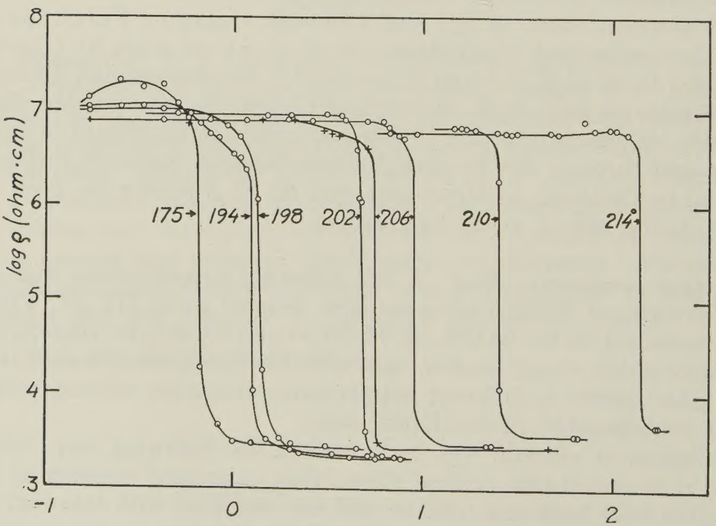


Fig. 1 and Fig. 2. Variations of the resistance during the crystallization.

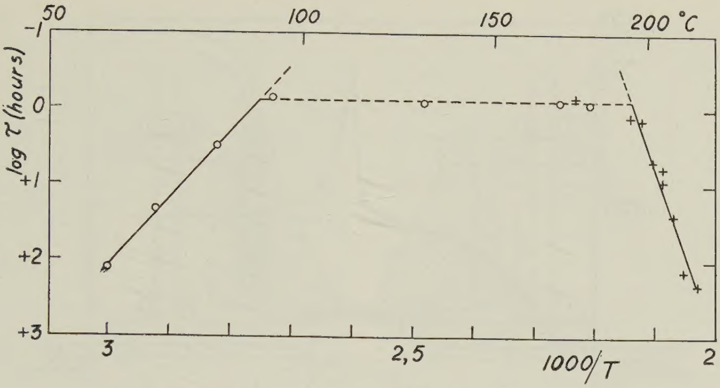


Fig. 3. Logarithm of time for crystallization (increasing downwards) as a function of temperature.

rangements were those described in an earlier paper (2). The selenium was contained in glass bulbs about 2 cm in diameter, with platinum electrodes. Constant temperatures were obtained with vapour thermostats. Examples of curves showing the large decrease of the resistivity ϱ during the crystallization as a function of the time t at different temperatures are given in the log ϱ — log t diagrams in figs. 1 and 2.

As a measure of the crystallization times it is convenient to take some point on the steep part of the curves. We have chosen the time τ_1 when the resistivity has a value 10 times the value of the fully crystallized specimen. In fig. 3 the logarithms of these τ_1 are plotted against the reciprocals of the absolute temperatures. The diagram is so arranged that the increasing ordinate corresponds to increasing rate of crystallization. The rings refer to a specimen of Se III which was first quenched from the liquid state to room temperature and then heated. The crosses refer to a specimen of Se IV which was directly cooled from the liquid state to the measuring temperature. In the diagram can be distinguished three different ranges of crystallization, one below 90° C, one from about 90° to 190°, and one from 190° to the melting point. As will appear from the following, these ranges roughly coincide with the microscopically observed ranges for the growths of spherulites, branched crystals and grains.

At low temperatures the velocity of crystallization increases rapidly with increasing temperature. At high temperatures, slightly below the melting point, the velocity again decreases rapidly when the temperature approaches the melting point.

The intermediate range of temperature in which the time of crystallization is seemingly independent of the temperature, is a phenomenon often observed in earlier investigations on the crystallization of various substances, and there has been much discussion about its interpretation. At least in our case, the phenomenon is connected to an increase of the temperature of the specimen, caused by the heat evolved during the rapid crystallization and dependent on the dimensions of the specimen and its thermal contact with the surroundings. A simple thermal analysis experiment gives an idea of what really happens. A glass bulb with a specimen of amorphous selenium of similar dimensions to the specimens for resistance measurements and having initially room temperature, was put into an oven, the walls of which had a temperature of 95° C. The temperature of the specimen was measured

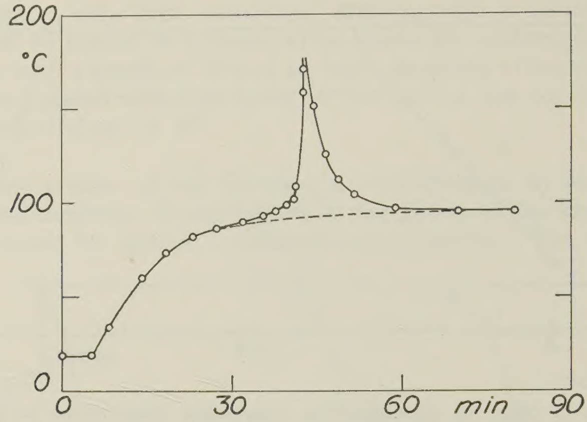


Fig. 4. Variations of the temperature due to the evolution of heat during the crystallization.

by a thermocouple, embedded in the selenium. The measurements gave the temperature-time curve shown in fig. 4. If there had been no evolution of heat of crystallization, the temperature would have approached the surrounding temperature (95° C) asymptotically from below. The crystallization, however, causes a temporary increase of temperature up to a temperature not very far from the melting point. The phenomenon is rather complicated and besides the factors already mentioned, the increasing rapidity of crystallization with the temperature at lower temperatures and the decreasing rapidity near the melting point are also involved. It is obvious that on the horisontal part of the curve in fig. 3, the temperatures of the specimen are not at all those of the surroundings used as abscissa, and that the horisontal line of the figure is not characteristic of the crystallization phenomenon itself.

Even in the ranges below 90° and above 200° C, where the temperature of the specimen does not differ very much from that of the surroundings, the crystallization phenomenon is complicated as it depends, as is well known from the work of TAMMANN (5) and others, on two different phenomena, the formation of crystal nuclei and the rate of crystal growth. As will be shown in the following, we have found other experimental ways of studying these two phenomena separately.

§ 4. Types of crystallization observed with a crystallization microscope on thin transparent layers at elevated temperatures. Circumstances are favourable for microscopic studies of the crystallization in selenium with transmitted light. Thin layers of liquid or amorphous selenium as well as thin layers of a selenium crystal are transparent to red light, whereas fine-grained crystalline specimens are untransparent. Further the melting point of selenium at 221° C is just sufficiently low to permit a heated specimen holder with fused selenium to be placed near a microscope without spoiling the lens systems of ordinary objectives. We have taken advantage of these circumstances by using a crystallization microscope, the construction of which is shown in fig. 5. Above the upturned objective of a metal microscope there is first a sheet of mica and a copper plate with a central hole. On this plate are placed two thin glasses (ordinary covering glasses) with the selenium specimen between them. On top of the upper glass there is an electrically heated copper cyl-

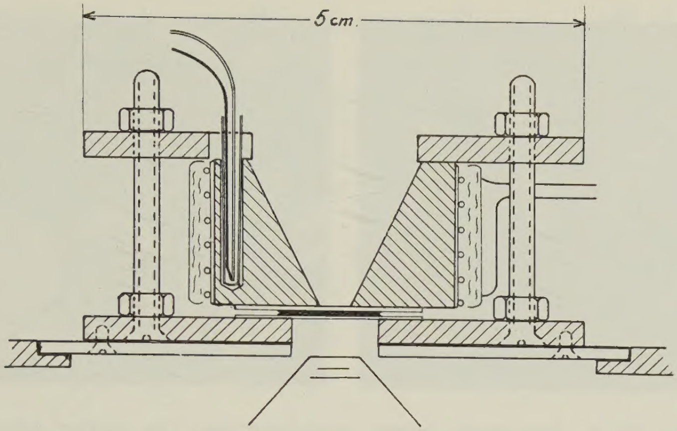


Fig. 5. Crystallization microscope.

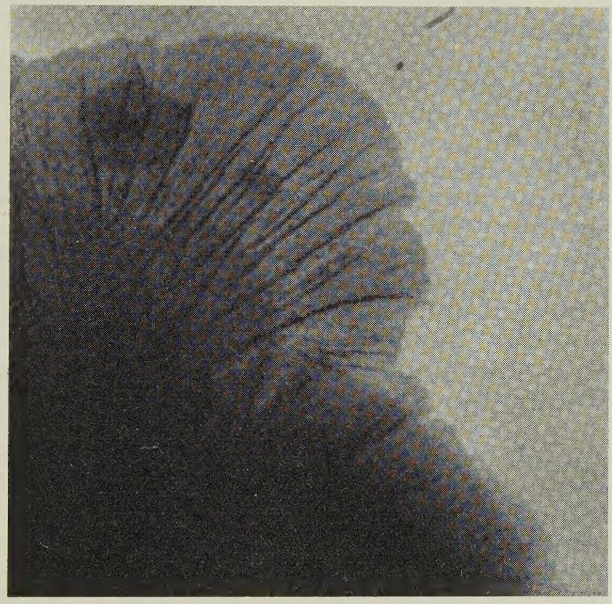


Fig. 6. Crystallization front × 500.

inder with a conical central hole admitting a converging beam of light to the specimen. The arrangement is held together with screws as shown in the figure. The temperature is measured by a thermocouple, one junction of which is put into a hole in the copper cylinder, and the other into melting ice. As the temperature of the selenium specimen is not exactly the same as that of the copper bloc, the thermocouple is calibrated by observing the electromotive force when selenium and some other suitable substance such as o-nitro-benzoic acid are melting between the glasses.

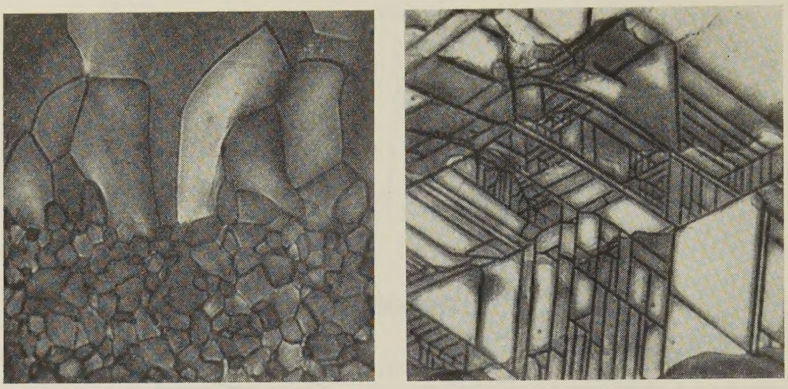


Fig. 7 and Fig. 8. Transparent layers crystallized near the melting point × 160.

The spherulites and single crystals, the latter often in the form of thin needles, grown at low temperatures, appear dark on the light background. The same is the case with the crystallization fronts advancing in the layer at higher temperatures up to about 200° C. In some cases the front is dark and sharp, in other cases it is preceded by a somewhat lighter border as in fig. 6. The dark lines to be seen in this border perpendicular to the front, are probably furrows due to a contraction of about 15% in the volume in connection with the crystallization.

Crystallization near the melting point gives transparent crystal plates with varying patterns of puckers. The larger grains in fig. 7 have grown at a temperature nearer the melting point than the smaller ones. In the case shown in fig. 8 the furrows are at angles of sixty degrees, which suggests that the hexagonal axis in this case is perpendicular to the covering glasses.

§ 5. Determination of the rate of dendritic crystallization by microscopic investigation on transparent layers. With the aid of the microscopic arrangement described in § 4 we have measured the rate of advance of crystal fronts such as shown in fig. 6, directly on an eyepiece scale turned perpendicularly to the front. The measurements cover a range of temperature from about 70° C up to immediately below the melting point. It was found that the linear velocity of crystallization thus obtained at the same temperature varied widely, not only for different specimens but also for different fronts of the same specimen. The highest and lowest velocities observed at the same temperature varied more than 70 to 1. It has been possible, however, to obtain series of comparable measurements for the determination of the dependence on temperature, either by studying the same front at several temperatures after one another or by removing the crystallization by raising the temperature momentarily just above the melting point. Some of the widest and best series are shown in fig. 9, where the logarithms of the velocity w are plotted against the reciprocal of the absolute temperature.

With the exception of the range near below the melting point the logarithmic curves are parallel to each other within the limits of experimental uncertainty, which means that the velocities of different series differ only by a constant factor independent of the temperature.

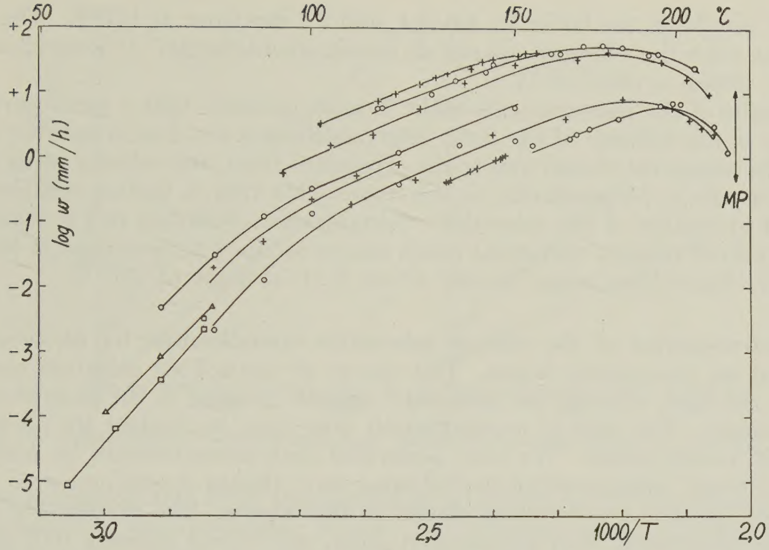


Fig. 9. Logarithm of crystallization velocities versus reciprocal of absolute temperature + and ○ from observations on crystallization fronts. □ from photometric, △ from microscopic observations on spherulites.

In order to establish the physical nature of the variations of this factor we have made extensive studies at a constant temperature of 147° C.

We first tried the hypothesis that the variations in velocity were due to various structures of the amorphous selenium. There could be some reason for this hypothesis in the peculiar resistance variations observed in liquid selenium in an earlier investigation (2). We obtained similar large velocity variations, however, by repeated microscopic tests on specimens taken from selenium heat-treated in many different ways or centrifugated in the molten state. From these experiments it was clear that various structural states of the amorphous selenium were at least not the only reason for the velocity variations.

We next searched, without result, for an influence from the intensity of the illumination of the specimen.

We finally tried the hypothesis that the variations in velocity should be due to different velocities of crystallization in different crystal directions. When sublimised from selenium vapour, selenium crystallizes as thin needles which, according to BRADLEY (6) and others, are parallel to the hexagonal axis and to the chains of atoms from which the hexagonal crystals are built up. This shows that in the case of sublimation the rate of crystal growth is greater in the direction parallel to the axis than in the perpendicular one. It should not be surprising if similar conditions were to be found in crystallization from the supercooled liquid. In order to try this hypothesis small fragments of crystal needles obtained by sublimation, were used as revealing crystals. They were brought into contact with the layer of supercooled selenium through a tiny hole in the upper covering glass either with their axis parallel to the layer or perpendicular to it. The experiment was difficult and only six successful series of measurements were obtained, two with the axis parallel and four with the axis perpendicular to the layer. The former gave the mean velocities

41 and 31 mm/hour, the latter 12, 4.0, 2.4, and 2.2 mm/hour at 147° C. The highest and lowest velocities obtained among all measurements at 147° C were 52 and 0.70 mm/hour, giving a ratio of 74 : 1.

The results of the measurements make it most probable that a great part of the variations in the velocity of the front of crystallization are due to varying orientations of the hexagonal crystal axis to the crystalline front, the velocity being a maximum if the axis is perpendicular to the front. This view is further completed and confirmed by studies of the spherulitic crystallization described in § 9, which show that the ratio of velocity variations which can be ascribed to variations in the structure of the amorphous state, is only about 3 : 1 at least at 70° C.

§ 6. **Determination of the rate of spherulitic crystallization by photometric investigation on transparent layers.** Thin layers of amorphous selenium are transparent to red light, whereas the spherulitic crystals growing in the amorphous matrix are opaque. The rate of crystallization may thus be studied by photometric absorption measurements. We have performed such measurements by means of a Pulfrich "Stufen" photometer in the following way. Grains of selenium were weighed and melted between two covering glasses to thin sheets. The thickness x of these sheets was determined from weights and areas, and varied between 0.02 and 0.11 mm. The light absorption of such a specimen was measured, in comparison with a standard specimen, at first in the rapidly cooled, amorphous state and then after repeated heating at a constant temperature (mostly 54, 62, 70, or 78° C). The measurements give the connection between the heating times t and the quantity I/I_0 where I_0 and I are the intensities of transmitted light before and after a certain heat treatment.

After some trials and with the guidance of theoretical considerations, it was found that, after a short initial period, the results could be described by the formula

$$\ln \frac{I_0}{I} = a + b t^2 \tag{1}$$

where b is a constant and a is either zero or a positive constant. Fig. 10 shows on four examples out of some fourty series of measurements, how $\ln I_0/I$ varies linearly with t^2.

The first rapid rise of the curves giving the constant term a in (1) could be ascribed to a non-spherulitic crystallization often observed in the microscope, occurring together with the spherulitic one, and producing in certain cases small crystal grains, in other thin crystal needles growing rapidly to a final size.

The following linear part of the curves seems to be due to the growth of the spherulites. Eq. (1), valid for this part, can be interpreted on the simple assumptions, which are also in good agreement with direct microscopic observations, that all spherulites of a specimen start within a short time and grow at the same linear rate, so that at a certain time they are all of nearly the same size.

We shall first calculate the case of only spherulitic crystallization. If the rate of linear growth is w cm/s the radius after heat treatment during t seconds is $r = wt$, and the total projected area of all the n spherulites in one cm³ is

$$A = n \pi w^2 t^2. \tag{2}$$

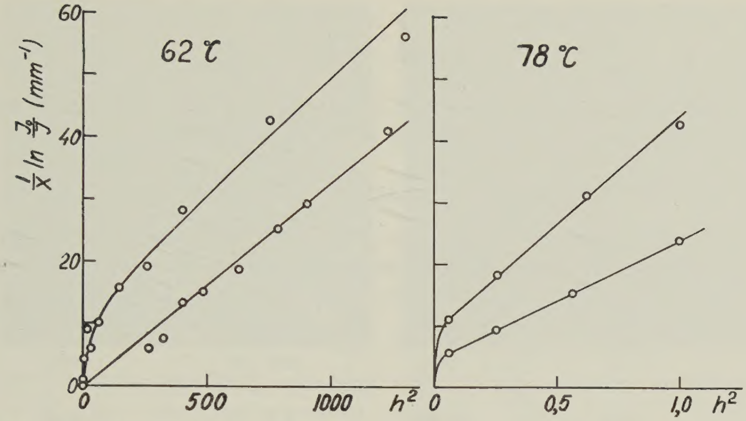


Fig. 10. Logarithm of (decreasing) light intensities versus square of heating time.

The total projection area of all the spherulites in a thin layer, the thickness of which is a fraction x of one centimeter, is $x A$. The circular, opaque areas of the single spherulites partly overlap leaving a transparent fraction of the layer given by I/I_0. During the time between t and $t + dt$ the total projected area of all the spherulites per cm^2 of the layer is increased by $x\,d\,A$, whereof the fraction I/I_0 decreases the transparent part of the layer by $d\,(I/I_0)$. Thus we have

$$d\frac{I}{I_0} = -\frac{I}{I_0}\,x\,d\,A\,. \tag{3}$$

The integration of this differential equation with respect to the condition $I = I_0$ for $A = 0$ gives

$$\ln\frac{I_0}{I} = x\,A \tag{4}$$

and because of eq. (2)

$$\ln\frac{I_0}{I} = x\,n\,\pi\,w^2\,t^2. \tag{5}$$

If there is also the other type of crystallization, which is completed already before the spherulitic crystallization becomes appreciable, we have when extrapolating to $t = 0$ not $I = I_0$, but $I = I_0'$ where $I_0' < I_0$, and we obtain instead of (5)

$$\ln\frac{I_0}{I} = \ln\frac{I_0'}{I'} + x\,n\,\pi\,w^2\,t^2. \tag{6}$$

This is our theoretical interpretation of the empirical formula (1). From the empirical constant

$$b = x\,n\,\pi\,w^2 \tag{7}$$

the linear crystallization velocity

$$w = \sqrt{\frac{b}{\pi\, x\, n}} \tag{8}$$

may be calculated, the product $x\,n$ which is the number N of spherulites per square centimetre of the layer being determined in the microscope.

Table 1

Photometric determination of the rate of spherulitic crystallization velocities.

Number	Temperature of crystallization °C	Thickness of specimen cm	Number of spherulites per cm^3	Velocity of crystallization μ/h
1	54.0	0.0049	$3.0 \cdot 10^9$	0.0083
2	62.0	0.0050	$2.5 \cdot 10^9$	0.065
3	70.0	0.0050	$2.4 \cdot 10^9$	0.38
4	78.0	0.0059	$2.8 \cdot 10^9$	3.2
5	78.0	0.0059	$0.84 \cdot 10^9$	2.4

Table 1 contains results of the determinations of the linear crystallization velocities of the spherulites at four temperatures of specimens taken from the upper part of rods obtained by centrifugating selenium VII during 6 hours at 250° C. The specimens nos. 1 to 4 were from the same rod, number 5 from another. These specimens had rather pure spherulite crystallization. The constant a in the empirical equation (1) was in all cases except no. 4, zero within the limits of errors. These results are also shown together with other results on crystallization velocities, in fig. 9 of § 5.

From the observed thicknesses x of the layers (which are of no influence on the calculations of the velocities) and the observed numbers N of spherulites per cm^2 we calculate the apparent numbers $n = N/x$ of spherulites per cm^3 given in the Table. These numbers are a few times larger than the largest numbers determined by means of the reflexion microscope (§ 9). We have the impression that some of the spherulites originate from the glass plates and are thus not characteristic of the selenium itself.

§ 7. **Types of crystal structures observed by means of reflexion microscopy.** When selenium is cooled rapidly from above the melting point to room temperature, it is obtained in the vitreous state, and polished specimens show no structural details in a metal microscope. After heating the specimen for, say some hundred hours at 50° C or about an hour at 75° a spherulitic crystallization normally appears, which is particularly distinct in polarized light. Figs. 11 and 12 show two types of spherulites in the amorphous mass, obtained after different treatment of the liquid. Fig. 13 shows the spherulites in greater magnification and at a later stage when all spherulites have grown into contact with each other. The spherulites are probably built up by a large number of small crystal needles of a size less than 0.01 mm.

Although at crystallization temperatures below 90° C the spherulites dominate, we have in some cases also observed single crystals in the amorphous mass. It is possible, however, that these isolated crystals have grown from nuclei formed

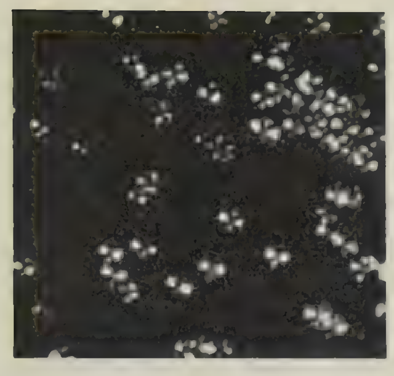


Fig. 11. Spherulites grown 15 hours at 70°. Low velocity of crystallization. Polarized light × 360.

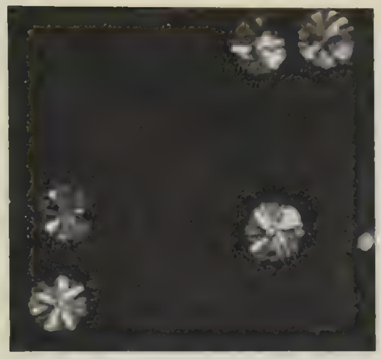


Fig. 12. Spherulites grown 16 hours at 70°. High velocity. Polarized light × 360.

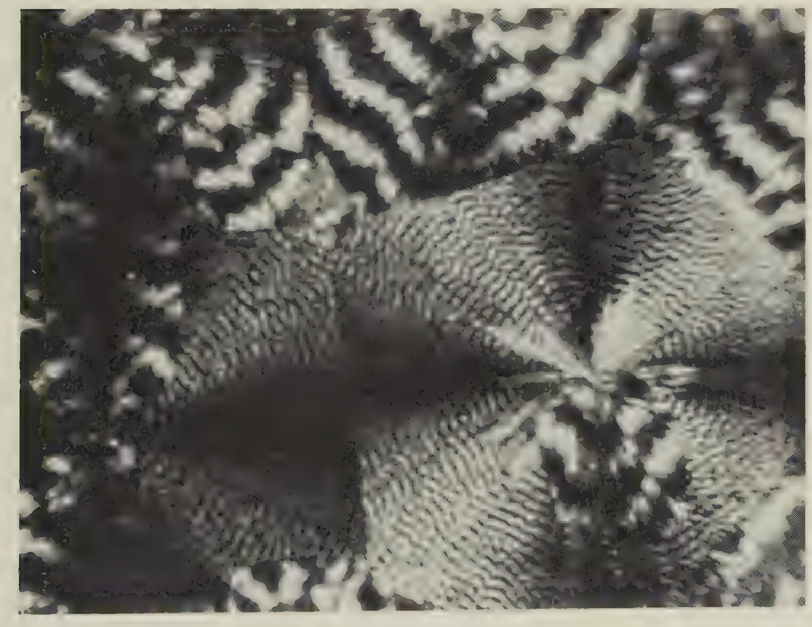


Fig. 13. Spherulitic crystallization at 70° C. Polarized light × 760.

at higher temperatures, during the cooling of the specimen from the melting point, whereas we have good reason to believe (cf § 9) that the spherulites are incited first at lower temperatures.

After heating amorphous selenium to temperatures between about 90 and 190° C there appears in the reflexion microscope especially when using polarized light, various branched crystal structures, of which Fig. 14 gives an example. As was shown in § 3, the crystallization in this range is influenced by a local increase of temperature, caused by the latent heat of crystallization.

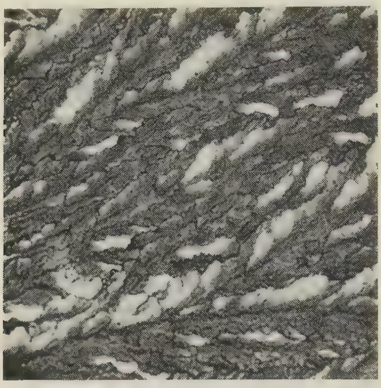


Fig. 14. Branched crystallization at 200° C. Polarized light × 330.

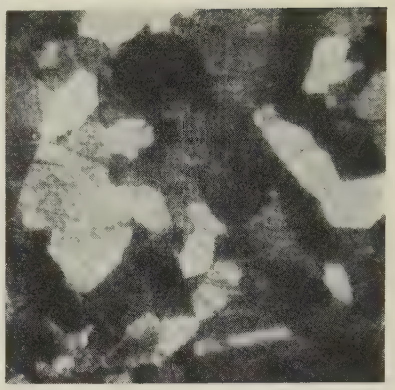


Fig. 15. Crystallization near the melting point. Polarized light × 700.

Crystallization between about 190° C and the melting point at 221° C leads to the formation of grains, the size of which is larger, the higher the temperature. Fig. 15 gives an example.

§ 8. **The influence of heat treatment on the rate of growth and number of spherulites, studied by reflexion microscopy.** The use of the metal microscope enables quantitative determinations of the rate of growth of the spherulites and their number per unit volume.

The linear velocity of growth w is obtained from the diameter D of a spherulite grown in a time t as

$$w = \frac{D}{2t}. \tag{9}$$

Quenched amorphous specimens are heated during a time t at a suitable temperature, cooled, cut, polished, and examined in the microscope. The diameters of the largest round spots to be seen in the microscope are measured by an eyepiece micro-

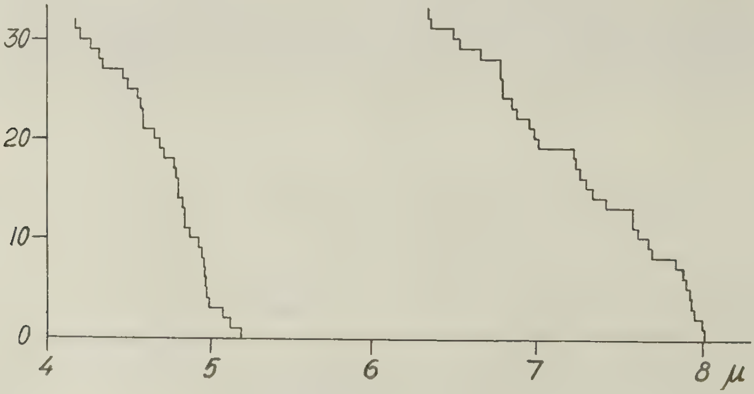


Fig. 16. Distribution of radiae of spherulites.

meter and give the diameters for calculating w. To obtain the best maximum values of D we have, as shown in fig. 16 plotted the number of spots within a certain area, which have diameters larger than a given value, as ordinates against the diameters as abscissae. In most cases the distribution function gives a sharp maximum limit of D. In some cases one or two observations which deviate from the normal distribution, have been disregarded in determining this limit.

To obtain the number n of spherulites per cm^3 from the number N of spots observed within a certain area A cm^2, it is necessary to know the diameters and their distribution function. The fact that all the spherulites in a transparent layer heated at a constant temperature, seem to be of nearly the same size, as well as a study of the distribution of the diameters of the spots on polished surfaces, seem to indicate that most spherulites have begun to grow at an early stage of heating. If all the spherulites had the same size, those visible on the polished surface should have their centres within half the diameter's distance on both sides of the surface and we should have

$$n = \frac{N}{A\,D}. \tag{10}$$

If some of the spherulites have diameters less than the maximum ones the number n calculated according to eq. (10) would be too small. This simple calculation will do, however, for a preliminary study of the large variations of n for specimens of different origin and varying heat treatments.

For these purposes we have studied specimens from five different makes of Boliden selenium. The specimens were prepared in the following way. A glass tube with selenium was heated under continuous evacuation from room temperature to some chosen temperature above the melting point, sealed and kept in the oven for a chosen time and thereafter rapidly cooled to room temperature in order to obtain specimens in an amorphous state. All the specimens were then heated for 10 to 20 hours at 70.0° C in order to obtain spherulites of suitable size for microscopic measurements. The observed crystallization velocities, calculated according to (9) have varied between the limits 0.25 and 0.8 microns pro hour at 70° C. The number of spherulites has been from 1—1 000 millions per cm^3.

We shall here give a brief survey of the results, which are, however, only preliminary, and to a main part obtained during the last few months from series of measurements which are not yet finished.

Extended heat treatment at 250° C seems to give low velocity of spherulitic crystallization. Se VII gave values of w from 0.29 to 0.25 μ/h at 70° C. Se IX gave values decreasing from 0.30 to 0.23 in 200 hours, Se VIII gave $w = 0.42$ after 24 hours of heating, and 0.35 after 213 hours. Probably there is an equilibrium velocity, at about 0.2 μ/h.

The same specimens Se VII, VIII and IX when heated during 102 hours at 550° C, gave high velocities of crystallization, namely $w = 0.68$, 0.70, and 0.73 μ/h at 70° C.

The figures 11 and 12 give a comparison between spherulites grown under the same conditions in selenium heated at 250 and 550° C respectively.

Though it is evident from these results that there is a variation of the structure of liquid selenium with the temperature, our measurements in the intermediate range of temperature are not yet sufficient to decide whether the equilibrium structure varies continuously with the temperature, or if there is some kind of transformation point. Another question that we hope to have answered in the near future is whether and how the variations in velocity of crystallization are connected to the variations in resistance and density described in an earlier paper (2).

The number of spherulites developed at 70° C has varied widely for different specimens and heat treatments. The greatest numbers after heating at 250–260° C have been for Se III 7, for Se VI 2, for Se VII 900, for Se VIII 60, and for Se IX 160 millions per cm^3. The number of spherulites in the specimens heated at 550° was much lower. A specimen obtained by distillation at 360° showed no spherulites at all.

The only effect we have so far observed from the centrifugation experiments is that the centrifugation seems to promote the homogenization of the sample.

The precaution to have the specimens enclosed in evacuated glass tubes seems to be rather important for the study of the spherulites. Specimens kept in touch with the atmosphere often show a non-spherulitic crystallization penetrating from the surface.

§ 9. **Temperature dependence of the rate of growth and number of spherulites.** We have two series of measurements on the variations of spherulitic crystallization velocities with temperature. One series was obtained, as already described in § 6, by means of the photometric method on specimens of the rather slowly crystallizing Se VII. The results are given in Table 1. The other series was carried out by means of the metal microscope on the more rapidly crystallizing Se III at 60, 70 and 80° C. The specimens were all prepared in the same way. A glass tube with the selenium powder was evacuated, sealed, heated for 21 hours at 260° C, quenched to room temperature and then heated for various times in a water vapour thermostat at the given temperature and again quenched. The glass tube was then broken and the specimen, which had a diameter of 8 mm and a length of 30 mm or more, was taken out, cut and polished, whereupon the maximum diameters were measured in a metal microscope at a magnification of about 120. The results for the three temperatures are given in the three diagrams of fig. 17. The scales for the radiae on the ordinate axis are the same, but the scales for the times on the abscissa axis are suitably varied. The experimental points are best satisfied by slightly bent curves. If there really is a decrease of the crystallization velocity with time or if the bendings are a result of accidental variations in the properties of the specimens, cannot be decided without further experiment. The initial values obtained for w are

at 60.0° C	$w = 0.107$ μ/h
» 70.0° C	0.74 »
» 80.0° C	3.75 »

These results are also shown together with the other results on crystallization velocities in fig. 9 of § 5.

Qualitative experiences show that the number of spherulites developed at different temperatures in specimens of the same delivery, and similar heat treatment, decreases with increasing temperatures, and above about 140° C we have observed no spherulites at all. The measurements on Se III heated for 21 hours at 260° C gave as mean values of the number of spherulites in millions per cm^3 at 60° C 9.1, at 70° C 6.4, at 80° C 4.5. At 100° C the centres of crystallization were about 1 and at 130 about 0.1 millions per cm^3.

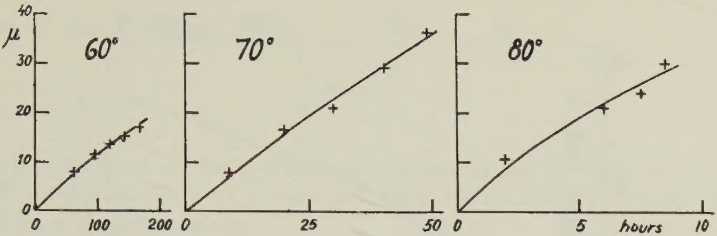


Fig. 17. Growth of spherulites at 60, 70 and 80° C.

§ 10. **Crystallization velocity and internal friction.** Already TAMMANN (7), in connection with his fundamental work on crystallization suggested that the decrease of crystallization velocity of a supercooled liquid with decreasing temperature might be connected with the increase in internal friction. A quantitative relationship between the linear velocity w and the coefficient of internal friction η has been derived by FRENKEL (8) and RICHARDS (9) who from different conceptions of the liquid state both arrived at the simple formula

$$w = \text{const.}\,\frac{1}{\eta} \tag{11}$$

where the constant has to be independent of temperature. The formula has so far not been fully substantiated by experiment. It was tested by RICHARDS on glycerine and by LEONTJEWA (10) by comparing results of different authors on crystallization velocities and internal friction in certain kinds of glass. In both cases it is questionable, however, whether the range of temperature of the comparison has been suitable. Immediately below the melting point the crystallization velocity is influenced by phenomena not taken into account in the deduction of the simple equation (11).

For the case of selenium we have now obtained better means for a comparison. It is true that in the range of temperature from about 50° C to the melting point, where we have made our measurements on the crystallization velocity, there are no measurements on the internal friction of the amorphous selenium, and probably such measurements would be difficult to make and unreliable because of disturbances from the crystallization process. There are, however, measurements on η as well above the melting point by DOBINSKI and WESOLOWSKI (11) and in a narrow range of temperature near 30° C, where the crystallization is slow enough not to disturb the measurements, by JENCKEL (12). In fig. 18 we have put together curves of log w from our measurements with curves of log $1/\eta$ from the mentioned authors as functions of the reciprocal of the absolute temperature. For log w we have chosen from the group of curves of fig. 9 a curve fitting the measurements on spherulitic crystallization. The range immediately below the melting point where the curves in fig. 9 deviate from the straight lines, are excluded from the comparison for reasons which will be discussed in § 11.

At high temperatures the slopes of the straight curves for log w and log $1/\eta$ are the same and thus the equation (11) is valid here. The origins of the two logarithmic scales are chosen so that the continuations of the two curves coincide, giving a common straight line. At low temperatures there is evidently a deviation from this line for log $1/\eta$ as well as for log w and in fact it is possible to draw a simple common

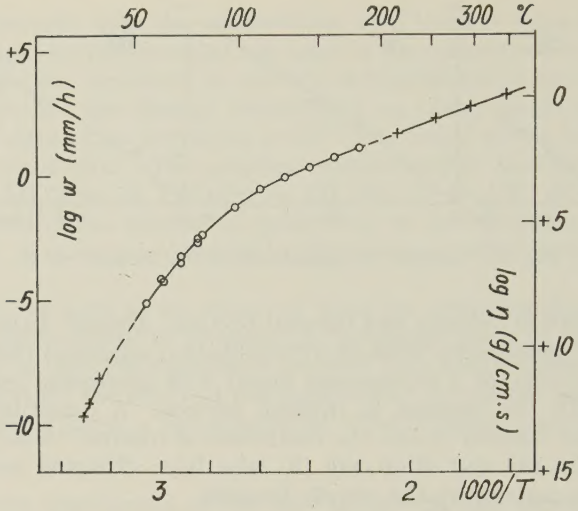


Fig. 18. Logarithm of crystallization velocity (circles) and logarithm of reciprocal viscosity (crosses) versus reciprocal of absolute temperature.

curve fitting the experimental result within the limits of probable error over the whole range of temperature. It is thus most probable that the simple equation (11) has a very general validity, at least in the case of a simple substance as selenium.

§ 11. **Discussion of the results on the temperature dependence of the crystallization velocity.** A discussion of the temperature dependence of the velocity of crystallization from a theoretical point of view has to consider the three different parts of the curves of fig. 9: 1) the middle linear parts between about 120 and 170° C, 2) the parts immediately below the melting point, and 3) the parts at low temperatures.

1) The parallel linear parts of the curves correspond to velocities obeying the empiric equation

$$w = A \cdot 10^{-\frac{B}{T}} \tag{12}$$

where A and B are constants or

$$w = A\, e^{-\frac{Q}{RT}} \tag{13}$$

where Q is the activation energy and R the gas constant. The activation constant $B = 3\,600$, which, as shown in § 10, is the same as for the internal friction, gives an activation energy of 69 000 joule/mol or 16 500 cal/mol. The empiric values of the constant A, i. e. the limiting velocity for high temperatures, are from $10^{4.2}$ to $10^{5.7}$ cm/s. These values are of the order of magnitude that could be expected theoretically. At very high temperatures one has to expect the crystal front to advance a distance of the order of the distance between neighbouring atoms δ in a time of the order of the period of atomic vibrations $\tau = 1/\nu$, where ν is the vibration frequency. That is

$$A \approx \delta \cdot \nu . \tag{14}$$

The value of δ may be taken from

$$\frac{\pi}{6}\delta^3 = \frac{V}{N} \tag{15}$$

where $V = 19.4$ cm³/mol is the volume of a gram atom (at 160° C) (4), and $N = 6.03 \cdot 10^{23}$ is the number of atoms per mol, which gives $\delta = 3.95 \cdot 10^{-8}$ cm. A mean value of ν is obtained from

$$\frac{h\nu}{k} = \theta \tag{16}$$

where $h = 6.55 \cdot 10^{-27}$ erg · s is Planck's constant, $k = 1.37 \cdot 10^{-16}$ erg/degree Boltzmann's constant, and $\theta = 230$ is the Debye characteristic temperature for selenium obtained from the specific heat at low temperatures (4). We thus obtain $\nu = 4.8 \cdot 10^{12}$ and

$$A_{\text{calc}} = \delta \cdot \nu = 1.9 \times 10^5 = 10^{5.3} \text{ cm/s} \tag{17}$$

where the empiric value of A goes from $10^{4.2}$ to $10^{5.7}$. The linear parts of the curves may thus be interpreted according to generally accepted theoretical views.

2) The decrease of the crystallization velocity when approaching the melting point is a well known phenomenon, quantitatively well understandable from a theoretical point of view (13). The net passage to the crystal is a difference between flows of atoms in both directions. In the simplest case both flows may be of the type described by eq. (12) and thus the crystallization velocity may be written

$$w = A_1 e^{-\frac{B_1}{T}} - A_2 e^{-\frac{B_2}{T}}. \tag{18}$$

Sufficiently far below the melting point the first term dominates and thus gives an approximation to equation (12). At the melting point the two terms just compensate each other and the velocity becomes zero. Equation (18) with the additional condition of $w = 0$ for $T = T_m$, the absolute temperature of fusion, gives curves of the general type found experimentally and shown in fig. 9. Our case is complicated, however, i. a. by different velocities of growth in different crystal directions, and, as the curves of fig. 9 seem to indicate, a quantitatively different effect of the approach to the melting point at high and low velocities. The phenomena are worth closer investigation from both the experimental and the theoretical side.

3) Whereas no serious alternatives to the qualitative interpretation of the linear slope of the curves in fig. 9 or of the extended curve in fig. 18 have been found, the interpretation of the increased slope at low temperatures is more uncertain. In some way the crystallization velocities, as governed by equation (12), with the constant values of the parameters A and B valid at higher temperatures, must be gradually put out of action at low temperatures, and the simplest assumption is that one of the parameters A or B or both of them become variable with decreasing temperature. On the basis of the experimental results obtained so far, it is not possible to choose between these alternatives by a purely mathematical discussion. The difficulties of separating temperature variations of A and B in expressions of the form of Eq. (12) are well known also from other parts of physics. Physically, however, variations in A and B mean different things.

If B is constant, A has to decrease with decreasing temperature in order to fit the observations. This means that the activation energy necessary for an atom to pass from the amorphous mass to the crystal is independent of temperature, whereas the number of atoms in a position to pass if getting the necessary energy, decreases with decreasing temperature. Such a case could be expected if only such atoms which are in a certain state of dissociation are able to move. Though the quantitative results do not seem to be compatible with any simple type of association process, there might be some complicated association processes connected with the chain structure of selenium.

If, on the other hand A is constant, B has to increase with decreasing temperature. This would mean that all or at least most of the atoms are a priori able to move though the activation energy necessary for movement increases with decreasing temperature. The lowest point of the curve in fig. 18 would correspond to an increase of B from 3 600 valid at high temperatures, to 5 800. Such a value is still conceivable as it is less than the activation constant of the vaporization from crystalline selenium, which according to NEUMANN and LICHTENBERG (16) is 7 440.

For the present we cannot choose between the thinkable alternative solutions of the problem.

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